

Environmental

Robust analysis of a variety of water and wastewater samples according to U.S. EPA Method 6020B (SW-846)

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Keywords

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iCAP RQplus, robustness, matrix
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Goal

To evaluate and demonstrate performance of the Thermo Scientific™ iCAP™ RQplus ICP-MS for robust analysis of a variety of wastewater samples according to the compliance requirements of U.S. EPA Method 6020B

Introduction

As a result of factors such as climate change, increasing population, and ongoing industrialization, various types of solid and liquid waste are being introduced or released into the environment, causing damage to the ecosystem. Though there are several preventive measures in place globally to control the entry of these waste materials into the environment and protect it from pollution, it is extremely difficult to reduce these anthropogenic contamination sources to zero.

The U.S. Environmental Protection Agency's (EPA) Office of Solid Waste and Emergency Response (OSWER) and Office of Resource Conservation and Recovery (ORCR) regulate all waste under the Resource Conservation and Recovery Act (RCRA). The RCRA's goals are to:

1. Protect the public from the hazards of waste disposal
2. Conserve energy and natural resources by recycling and recovery
3. Reduce or eliminate waste, and
4. Clean up waste that may have spilled, leaked, or was disposed of improperly.

The OSWER/ORCR publication SW-846, entitled “Test Methods for Evaluating Solid Waste, Physical/Chemical Methods”, is the EPA’s official compendium of analytical and sampling methods that have been evaluated and approved for use for analysis relating to the RCRA regulations. SW-846 functions primarily as a guidance document setting forth acceptable, although not required, methods for the regulated and regulatory communities to use in responding to RCRA-related sampling and analysis requirements. SW-846 is a multi-volume document that changes over time as new information and data are developed. It was first issued by the EPA in 1980 and is currently in its fifth edition.

As a part of a recent edition, this EPA method has been revised to EPA Method 6020B, which provides guidelines on target analytes, detection limits, sample collection, preparation and storage, and various quality control protocols to follow while performing such analyses.

This application note discusses a total workflow of the analytical method developed for analysis of water and wastewater samples using the iCAP RQplus ICP-MS, which offers a comprehensive solution for effective and trouble-free analysis of samples containing high dissolved solids, such as wastewaters and solid wastes. The Thermo Scientific™ Qtegra™ Intelligent Scientific Data Solution™ (ISDS) Software was used to control the iCAP RQplus ICP-MS instrument and to generate, process, and report analytical data, ensuring that the entire workflow meets the requirements described in EPA Method 6020B, including all the applicable QC checks. To verify the consistent performance of the instrument over time, a sequence of 200 samples was repeated over three consecutive days, so that 600 unknown samples were analyzed successfully.

Experimental

Instrument parameters and experimental conditions

The iCAP RQplus ICP-MS was used in this study. The instrument includes a full toolset to allow direct analysis of samples with increased levels of dissolved solids without prior, off-line dilution. This is accomplished through the automated addition of an argon diluent stream, provided by the iCAP RQplus ICP-MS instrument itself. To allow for unattended operation, the system was operated in conjunction with a Thermo Scientific™ iSC-65 autosampler. The sample introduction system was configured using components including a MicroMist™ nebulizer (400 $\mu\text{L}\cdot\text{min}^{-1}$), Ni-tipped sample and skimmer cones, cyclonic spray chamber, 2.5 mm quartz injector, and a quartz torch, as summarized in Table 1. The iCAP RQplus ICP-MS was operated in KED mode, using pure helium as the only collision cell gas to remove potential polyatomic interferences on various analytes. The typical instrument parameters selected during this study are also summarized in Table 1.

Table 1. Instrument configuration and typical operating parameters

Parameter	Value
Nebulizer	MicroMist nebulizer (400 $\mu\text{L}\cdot\text{min}^{-1}$)
Interface cones	Ni – tipped sample and skimmer
Skimmer cone insert	High matrix
Spray chamber	Cyclonic quartz
Injector	Quartz, 2.5 mm i.d.
Torch	Quartz torch
Auxiliary flow ($\text{L}\cdot\text{min}^{-1}$)	0.8
Cool gas flow ($\text{L}\cdot\text{min}^{-1}$)	14
Nebulizer flow ($\text{L}\cdot\text{min}^{-1}$)	0.26
AGD setting	Mid
Additional gas, argon (% of range)	65
RF power (W)	1,550
Number of replicates	3
Spray chamber temperature ($^{\circ}\text{C}$)	2.7
KED settings (gas flow rate in $\text{mL}\cdot\text{min}^{-1}$)	4.8 (with a 3V kinetic energy barrier)
Number of sweeps	5

The iCAP RQplus ICP-MS was automatically tuned using the built-in tune sequences to optimize all critical parameters, including parameters related to the sample introduction system and lens voltages. This readily available tune set helps all to set up and operate the instrument easily and to achieve the required sensitivity and matrix tolerance.

Prior to analysis, the instrument’s performance was verified using the automated performance check available within the Qtegra ISDS Software. In this test, the sensitivity across the mass range is checked for ^7Li , ^{59}Co , ^{115}In , and ^{238}U . Other plasma-related performance parameters, such as oxide formation and doubly charged ion formation rates, were also checked using the $^{140}\text{Ce}^{16}\text{O}^+ / ^{140}\text{Ce}^+$ and $^{137}\text{Ba}^{++} / ^{137}\text{Ba}^+$ ratios, respectively. As outlined in the EPA Method 6020B, other parameters including mass calibration and mass resolution were also checked during this test.

Standard and sample preparation

Diluent and calibration blank matrix

The diluent and calibration blank matrix were a mixture of 2% (v/v) nitric acid and 0.5% (v/v) hydrochloric acid in ultrapure water.

Calibration standards

To determine analytical figures of merit, such as instrument detection limits (IDLs), linear range, and correlation coefficients, calibration curves were generated for 24 analytes including seven calibration standards and a calibration blank. Multi-element linearity standards were prepared from aqueous single element solutions of each target analyte (1,000 mg·L⁻¹, SPEX CertiPrep™, Metuchen, NJ, USA). Three different stock solutions were prepared to accommodate analytes with different concentrations and chemical compatibility. The stock solutions were then diluted gravimetrically using 2% (v/v) nitric acid as a diluent to result in the concentrations specified in Table 2. An internal standard solution containing 1,000 µg·L⁻¹ of ⁶Li, 200 µg·L⁻¹ of Sc, and 20 µg·L⁻¹ of Y, Rh, In, Tb, Ho, and Bi was added on-line continuously during the entire duration of the analysis. All 32 analytes (including the internal standards) were measured using kinetic energy discrimination (KED) mode, with pure helium used as the collision cell gas.

Quality control standards (ICB, CCB, ICV and CCV)

The calibration blank containing mixture of 2% (v/v) nitric acid and 0.5% (v/v) hydrochloric acid in ultrapure water was used for Initial Calibration Blank (ICB) and Continuing Calibration Blank (CCB) QC verification during the analytical sequence. Two further QC samples, an Initial Calibration Verification (ICV) and a Continuing Calibration Verification (CCV), were prepared according to EPA Method 6020B. The solution used for ICV was prepared using an independent stock solution, whereas the CCV was prepared with the same stock solutions used in the preparation of the initial calibration solutions. The concentrations of all analytes in both ICV and CCV QC standard solutions were prepared as per the requirement outlined in EPA Method 6020B. Table 2 summarizes the list of analytes and their concentrations (given in µg·L⁻¹) in the different calibration solutions and ICV and CCV QC standard solutions.

Results and discussion

Linearity, instrument detection limits, LLOQ, and linear range

Instrumental detection limits (IDLs) for all analytes were calculated following the guidance provided in section 9.3 of EPA Method 6020B. The calibration blank was analyzed ten times, treating it as an individual sample each time. Subsequently, IDLs were calculated based on three times the standard deviation of the ten replicate measurements. Excellent detection limits were achieved for most of the analytes, except for the typical major analytes Na, Mg, Al, K, Ca, and Zn, which arise as common trace level contaminants in the reagents used in the experiments. The correlation coefficients (R²) obtained for all analytes were found to be greater than 0.9995, which suggests excellent linear response for the established concentration range for each analyte. The measured analytes, together with their masses (*m/z*), calibration correlation coefficients (R²), and IDLs are summarized in Table 3.

The lowest concentration standard from the set of calibration solutions was used to test the lower limit of quantification (LLOQ) for all analytes. The LLOQ values for each analyte were determined by analyzing seven replicate samples spiked at specified concentrations (Table 4). The mean recovery and RSD of seven replicates were confirmed to be 65–135% and less than 20%, respectively.

In alignment with Section 9.6 of EPA Method 6020B, standards containing analytes at concentrations higher than the highest calibration standard (Standard 5 for Hg and Standard 8 for all other analytes) were analyzed within the same run as the samples, following instrument calibration. The results from the analyses of these standards were within 10% of the true values, establishing the linear range which is the highest concentration that can be reported without diluting the sample. Hence, samples with analyte concentrations over the calibration range but within the established linear range did not require further dilution and reanalysis.

The linear range for each analyte is summarized in Table 4.

Table 2. List of target analytes and concentrations in calibration standards, ICV and CCV QC standards (µg·L⁻¹)

Analyte	STD 1	STD 2	STD 3	STD 4	STD 5	STD 6	STD 7	STD 8	ICV-QC	CCV-QC
Ag	0	0.1	1	5	10	50	100	500	7.5	10
Be, Ba, V, Cr, Mn, Co, Ni, Cu, Zn, As, Se, Mo, Cd, Sb, Tl, Pb, Ti	0	1	10	50	100	500	1,000	5,000	75	100
Na, Mg, K, Ca, Fe, Al	0	25	250	1,250	2,500	12,500	25,000	125,000	1,875	2,500
Hg	0	0.1	0.5	1	5	–	–	–	0.4	0.5

Table 3. List of analytes, *m/z*, correlation coefficients, and instrumental detection limits (IDLs)

Analyte	<i>m/z</i>	R ²	IDL (µg·L ⁻¹)	Analyte	<i>m/z</i>	R ²	IDL (µg·L ⁻¹)
Ag	107	0.9997	0.032	Mg	24	>0.9999	1.947
Al	27	>0.9999	1.63	Mn	55	0.9999	0.18
As	75	>0.9999	0.61	Mo	95	>0.9999	0.066
Ba	137	>0.9999	0.055	Na	23	0.9996	5.58
Be	9	>0.9999	0.001	Ni	61	0.9999	0.043
Ca	44	0.9998	8.12	Pb	208	>0.9999	0.008
Cd	111	>0.9999	0.017	Sb	121	>0.9999	0.103
Co	59	0.9999	0.004	Se	78	>0.9999	0.639
Cr	52	0.9999	0.056	Ti	48	0.9999	0.097
Cu	63	>0.9999	0.63	Tl	205	>0.9999	0.016
Fe	54	>0.9999	0.5866	V	51	0.9995	0.078
Hg	202	0.9994	0.06	Zn	66	>0.9999	0.256
K	39	0.9998	10.01				

Table 4. List of analytes and their established LLOQ concentrations and linear range

Analyte/Interferent	LLOQ (µg·L ⁻¹)	Linear range (mg·L ⁻¹)
Ag	0.1	2
Be, Ba, V, Cr, Mn, Co, Ni, Cu, Zn, As, Se, Mo, Cd, Sb, Tl, Pb, Ti	1	20
Na, Mg, K, Ca, Fe, Al	25	1,000

Interference check sample solutions (ICSA and ICSAB)

To ensure interference-free analytical measurements and to assess the accuracy of the developed analytical method, two separate solutions, commonly referred to as ICSA and ICSAB, were prepared and measured on each day of analysis. The concentration of the ICSA and ICSAB solutions selected for this study align with EPA Contract Laboratory (CLP) requirements. The ICSA solution contains all interferents at indicated concentrations, whereas the ICSAB solution contains both analytes and interferents. Table 5 summarizes the complete list of analytes and interferents and their concentrations in both the ICSA and ICSAB solutions.

Table 5. Analytes and interferents with their respective concentrations in ICSA and ICSAB solutions (all results expressed as µg·L⁻¹)

Analyte/Interferent	ICSA	ICSAB
Ag, As, Ba, Be, Cd, Co, Sb, Se, Tl, V	0	20
Cr	0	40
Cu, Ni, Pb	0	25
Mn, Zn	0	30
Al, Ca, Fe, Mg, K, Na, P, S	100,000	100,000
C	200,000	200,000
Cl	1,000,000	1,000,000
Mo, Ti	2,000	2,000

The percent recovery for all analytes including interferents in the ICSAB solution and percent recovery of only the interferents in the ICSA solution was calculated automatically within the Qtegra ISDS Software using the comprehensive quality control function. The percent recovery (% R) values obtained for all analytes in both the ICSA and ICSAB solutions on all three days of continuous measurement were found to be in the range of 90–110%, which is well within the acceptance criteria of ±20% (equivalent to 80–120%) of the true value. Table 6 presents analytes including interferents and their respective percent recoveries obtained in ICSA and ICSAB solutions on day 1.

Table 6. Percent recoveries (% R) obtained for all analytes in the ICSA and ICSAB solutions on day 1

Analyte	% Recovery		Analyte	% Recovery	
	ICSA	ICSAB		ICSA	ICSAB
Ag	N/A	108.6	Se	N/A	105.2
As	N/A	104.6	Tl	N/A	97.8
Ba	N/A	109.5	V	N/A	101.5
Be	N/A	94.6	Zn	N/A	102.1
Cd	N/A	98.7	Al	99.8	101.2
Co	N/A	104.1	Ca	98.8	99.7
Cr	N/A	103.1	Fe	99.2	100.3
Cu	N/A	105.6	Mg	100.1	101.4
Mn	N/A	99.7	K	98.5	99.6
Ni	N/A	105.8	Na	94.9	96.3
Pb	N/A	103.6	Mo	93.6	95.5
Sb	N/A	106.0	Ti	98.7	99.8

Quality control (QC) checks

EPA Method 6020B is a performance-based method that includes analysis of a series of QC samples as part of the quality control protocol to ensure accuracy, precision, robustness, and reliability of the analytical data acquired during the run sequence. The following sections describe the QC standards and samples that must be analyzed with each analytical run sequence.

Initial Calibration Blank (ICB)

A calibration blank solution containing a mixture of 2% (v/v) nitric acid and 0.5% (v/v) hydrochloric acid in ultrapure water was analyzed immediately after the initial calibration to monitor the analyte concentrations to ensure that there is no carryover between samples at levels above the acceptance criteria. As per the acceptance criteria given in section 10.5.4 of EPA Method 6020B, the ICB should not contain a concentration of the target analytes above half of the concentration specified as the LLOQ of each analyte. The observed concentrations of all analytes in the ICB solution were found to meet the acceptance criteria described in the method, which indicated that the analysis could be continued.

Initial Calibration Verification (ICV)

The ICV standard was prepared using independent stock solutions to yield concentrations of all analytes, as per the guidance provided in section 7.24 of EPA Method 6020B, and analyzed after initial calibration to confirm the accuracy of this calibration. The concentrations of all the analytes in the ICV solution were found to meet the acceptance criteria of 90–110% of the true value of each analyte given in Table 2. Figure 1 presents the accuracy results obtained for all the analytes in the ICV solutions measured for three consecutive days during analysis of unknown samples. Additionally, low-level and mid-level read-back standards were analyzed to verify the accuracy. The measured concentrations of all analytes found to be within the acceptable range of 80–120% and 90–110%, respectively.

Percent accuracy of analytes observed in ICV solution for three consecutive days of measurement

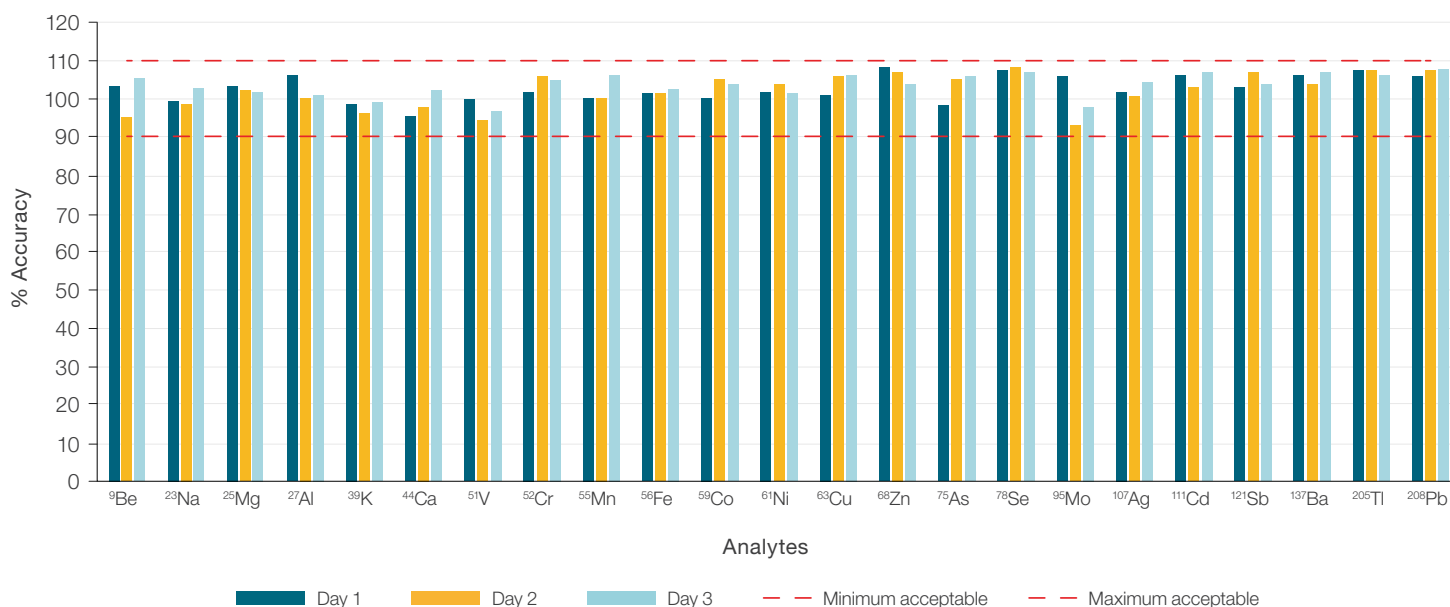


Figure 1. Percent accuracy of the ICV standard analyzed on three consecutive days

Continuing Calibration Blank (CCB)

To verify the ongoing validity of the initial calibration curve, the calibration blank was analyzed following every 10 unknown samples and at the end of each analysis batch, for batches analyzed over three consecutive days. The concentrations of all the analytes observed in multiple CCB solutions measured over the three days were found to be well below the LLOQ established for each analyte, which in turn suggests that the acceptance criterion was fulfilled and that the quality of the analytical data generated could be assured.

Continuing Calibration Verification (CCV)

In addition to the CCB check, a CCV standard was also analyzed every 10 samples to verify validity of the ongoing calibration. Concentrations of all the analytes in the CCV solution are presented in Table 2. The concentrations obtained for all the analytes in the CCV solution were found to meet the acceptance criteria of 90–110% of the true value of each analyte. Figure 2 presents the accuracy obtained for the analytes in the CCV solution for three consecutive days of measurements of unknown samples.

Matrix spike and duplicate measurement

To evaluate matrix effects and ensure accuracy and precision of the analytical measurement, a representative wastewater sample was analyzed in duplicate to investigate any bias and assess the precision of the measurement. The sample used in the study contains some analytes (specifically the major elements sodium, calcium and iron) at a level above the LLOQ, whereas most analytes are present at a concentration level below the LLOQ. For analytes that are above the LLOQ level, a spike recovery study was not performed, and the relative percent difference was instead calculated based on the values obtained in the original samples. For other analytes, the sample was spiked at the concentration levels indicated in Table 7. The spiked sample was then measured in duplicate to calculate the recovery and relative percent difference (RPD). The data obtained in this experiment suggested that the acceptance criteria mentioned in EPA Method 6020B for percent recovery and relative percent difference (RPD) of $\pm 25\%$ and $>20\%$, respectively, were met successfully. The percent accuracy values obtained during measurement of both matrix spike and duplicate samples were calculated automatically using QC functions MXS (Matrix Spike) and DUP (Duplicate) available in the Qtegra ISDS Software.

Table 7 summarizes the observed concentrations in both spiked and unspiked samples, spiked concentrations, relative percent difference (RPD), and average percent recovery calculated from duplicate sample measurements, for all analytes.

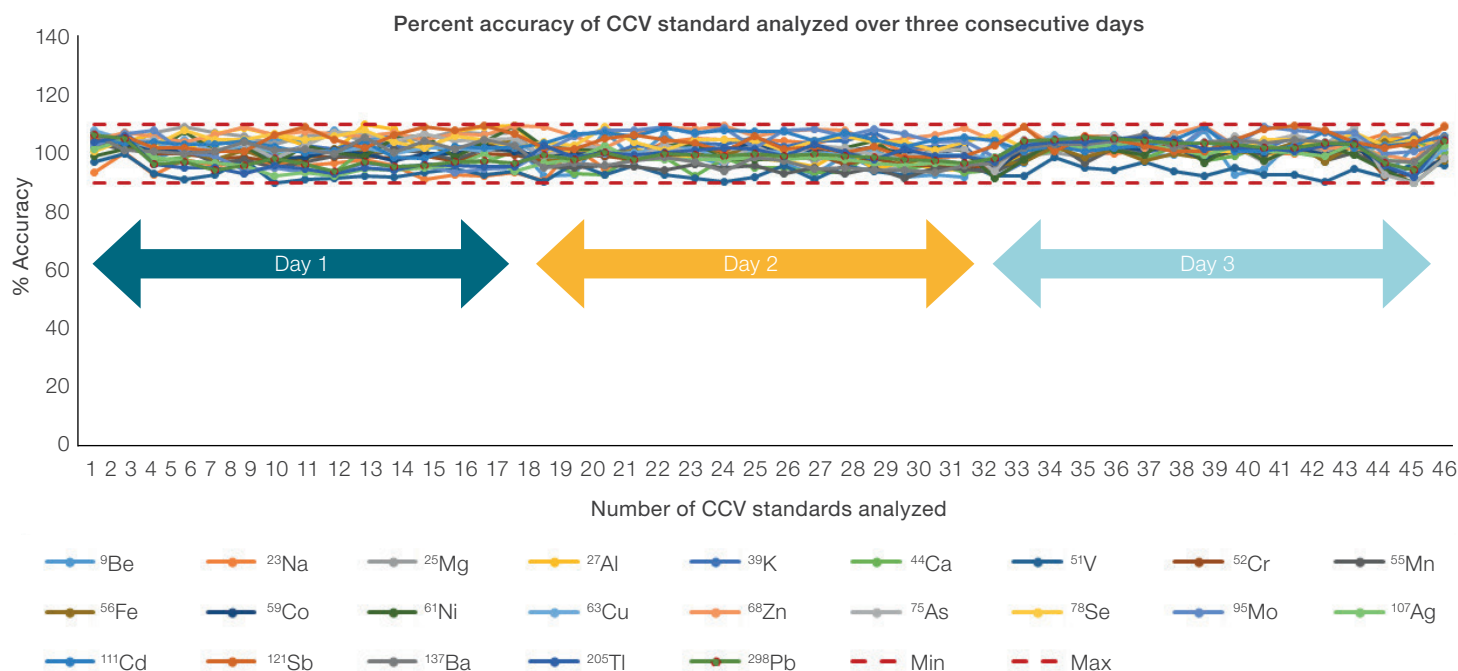


Figure 2. Percent accuracy of CCV standard analyzed on three consecutive days

Table 7. Analytes, their observed concentrations in un-spiked and spiked samples, spiked concentrations, relative percent difference (RPD), and average percent recovery

Analyte	Observed concentration (mg·L ⁻¹)		Spiked concentration (mg·L ⁻¹)	Observed concentration (mg·L ⁻¹)		% RPD	Average % recovery
	Sample 1 (unspiked)	Sample 2 (unspiked)		Sample 1 (spiked)	Sample 2 (spiked)		
Ag	<0.0001	<0.0001	0.02	0.021	0.021	2.4	103
Al	<0.025	<0.025	10	10.1	9.4	7.2	97
As	<0.001	<0.001	0.2	0.179	0.181	1.1	90
Ba	<0.001	<0.001	0.2	0.185	0.185	0.0	92
Be	<0.001	<0.001	0.2	0.221	0.196	12.0	104
Ca	455.2	451.6	N/A	N/A	N/A	0.9	N/A
Cd	<0.001	<0.001	0.2	0.174	0.171	1.7	86
Co	<0.001	<0.001	0.2	0.177	0.177	0.0	88
Cr	<0.001	<0.001	0.2	0.179	0.176	1.7	88
Cu	<0.001	<0.001	0.2	0.183	0.177	3.3	90
Fe	38.8	39.6	10	47.3	47.1	0.4	80
Hg	<0.0001	<0.0001	0.5	0.473	0.513	8.1	99
K	86.1	85.2	10	95.2	94.4	0.8	92
Mg	90.2	93.1	N/A	N/A	N/A	3.1	N/A
Mn	<0.001	<0.001	0.2	0.185	0.182	1.6	91
Mo	<0.001	<0.001	0.2	0.198	0.2	1.0	99
Na	175	169	N/A	N/A	N/A	3.7	N/A
Ni	<0.001	<0.001	0.2	0.184	0.183	0.5	91
Pb	<0.001	<0.001	0.2	0.176	0.177	0.6	88
Sb	<0.001	<0.001	0.2	0.192	0.188	2.1	95
Se	<0.001	<0.001	0.2	0.178	0.184	3.3	90
Tl	<0.001	<0.001	0.2	0.171	0.17	0.6	85
V	<0.001	<0.001	0.2	0.176	0.178	1.1	88
Zn	<0.001	<0.001	0.2	0.171	0.167	2.4	84

Method robustness – ensuring reliable analysis on consecutive days without any maintenance or downtime

Analysis of samples containing high amounts of total dissolved solids (TDS) leads to adverse effects in ICP-MS, such as matrix deposition on the interface cones, signal drift over time, suppression in the response of the internal standards, QC failures, and the need for more frequent maintenance of the instrument. All these challenges can ultimately mean that downtime is increased and that some samples may need to be re-analyzed, both of which cause a negative impact on the productivity of an analytical laboratory.

The major indicators of instrument robustness for extended analysis are consistency and minimum suppression in the internal standards response over a course of the analytical run. In this study, an internal standard solution containing Li, Sc, Y, Rh, In, Tb, Ho, and Bi was continuously added on-line using a Y-connector mixing block, and the response of the internal standards relative to the first blank of the initial calibration monitored. Figure 3 shows the response of all internal standards monitored in an analytical batch involving the measurement of a series of simulated water and wastewater samples for 10 hours. These simulated samples represent compositions of typical sample matrices such as surface water, ground water and brackish water. Figure 4 highlights the distribution of samples based on their percent TDS content.

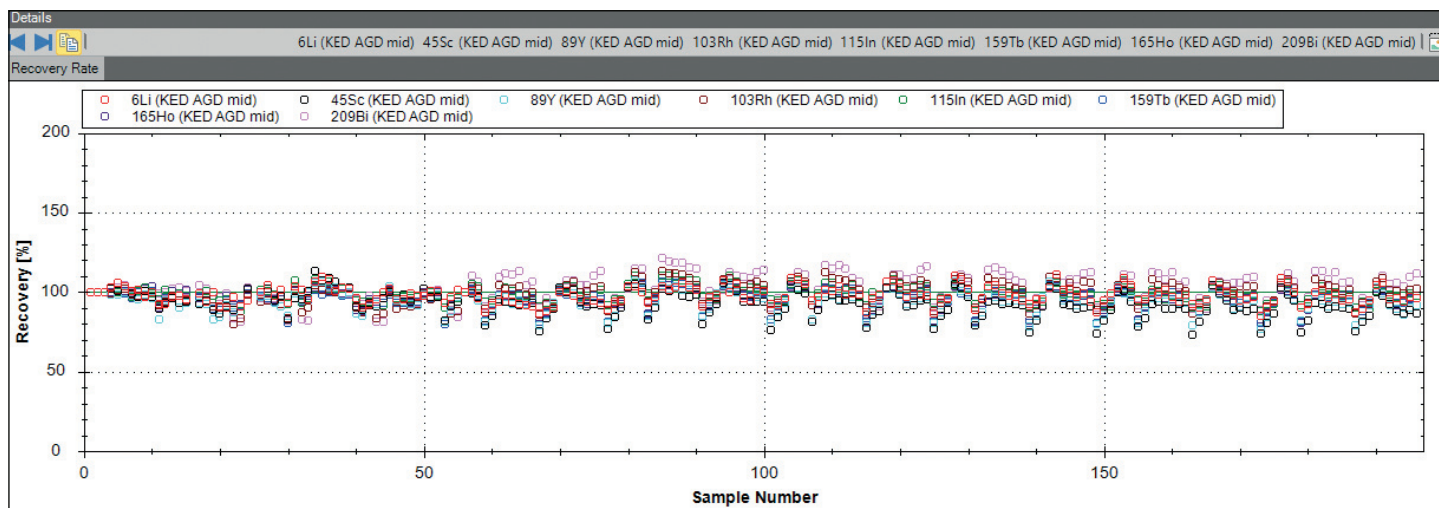


Figure 3. Internal standards response obtained over a period of 10 hours of continuous measurements

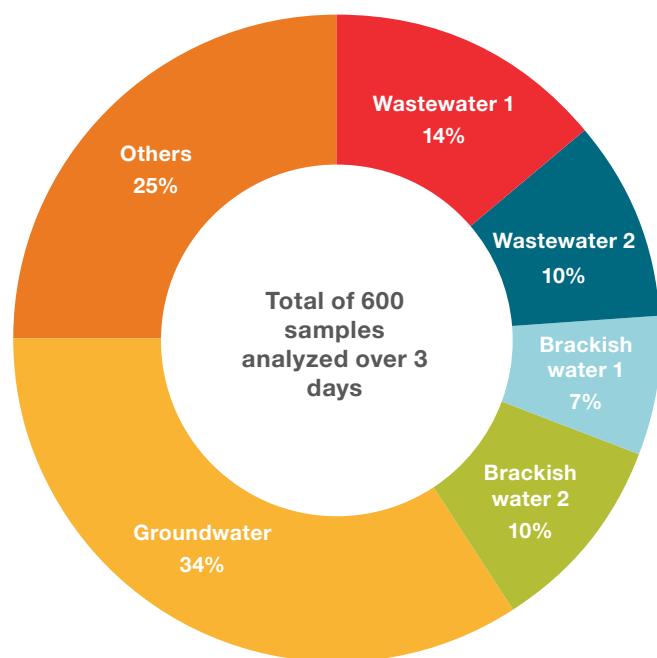


Figure 4. Distribution of all samples analyzed over three days based on their % TDS content

Figure 3 shows a screen image directly taken from the Qtegra ISDS Software as a representative example of the internal standard response observed on the second day of the consecutive measurements over three days. Similar behaviour was observed during the other two days. As can be seen, all internal standards read-back in a range between 75 to 125%, which is well within the acceptable range of $\pm 30\%$ described in EPA Method 6020B. Notably, maximum suppression (21%) was only observed for samples with the highest matrix load of 1.6% (m/v) total dissolved solids (TDS) and was still well within the acceptance criteria.

The unknown samples analyzed during each day were prepared to simulate the typical composition of groundwater, surface water, and wastewater samples with varying concentrations of typically observed elements, such as Na, Mg, K, Ca, Fe, and different anions. Commercially available 10,000 mg·L⁻¹ standard solutions and inorganic salts of these elements were used to prepare simulated samples. The anion concentrations were calculated based on the information available in individual certificates. Table 8 summarizes the composition and TDS content of various samples analyzed in this study. Figure 4 provides a distribution overview of the samples analyzed in this study over three consecutive days, based on their % TDS content.

Table 8. Composition and percent TDS content of various samples analyzed in the study

Sample name	Concentrations in mg·L ⁻¹							% TDS
	Na	Mg	K	Ca	Fe	Other transition metals	Anions	
Wastewater 1	2,000	2,000	2,000	2,000	1,000	1,000	6,000	1.6
Wastewater 2	1,000	1,000	1,000	1,000	500	500	3,000	0.8
Brackish water 1	5,000	500	100	100	0	0	9,000	1.47
Brackish water 2	2,500	250	50	50	0	0	4,500	0.735
Groundwater	200	200	200	200	200	0	1,500	0.25
Others	Blank, standards, and QC samples							N/A

Data acquisition, interpretation, and reporting

Data acquisition, interpretation, various QC calculations and reporting were all performed using the Qtegra ISDS Software, which also controls the overall operation of the iCAP RQplus ICP-MS. The intuitive and step-by-step guided workflow of the Qtegra ISDS Software enables the user to set up analytical run sequences with the required QC standards to generate analytical data in the desired reportable format.

The Qtegra ISDS Software has a built-in QC checking capability that is specifically designed to meet the requirements of EPA methods. Each QC type (ICV, CCV, ICSA, ICSAB, etc.) is

available as a default in the QC set-up page, and the user can define their own QC tests as required. Results in the software are visually flagged if they are outside the allowed range, which makes validation a simple process. Sample and spike recoveries are automatically calculated for any QC standard or spiked sample, and percentage recoveries can be calculated for duplicate samples (DUP) and matrix spike (MXS) samples. A variety of user-selectable automated actions can be set up to ensure that fully compliant analysis is achieved during an unattended run.

	Label	Survey Runs	Main Runs	Comment	Evaluate	Sample Type	Standard	Dilution Factor	Amount	Final Quantity	QC Action	QC Restart	QC Reference
1	Blank	0	3	<Comment>	✓	BLK		1			None		
2	STD 1	0	3	<Comment>	✓	STD	STD 1	1			None		
3	STD 2	0	3	<Comment>	✓	STD	STD 2	1			None		
4	STD 3	0	3	<Comment>	✓	STD	STD 3	1			None		
5	STD 4	0	3	<Comment>	✓	STD	STD 4	1			None		
6	STD 5	0	3	<Comment>	✓	STD	STD 5	1			None		
7	STD 6	0	3	<Comment>	✓	STD	STD 6	1			None		
8	STD 7	0	3	<Comment>	✓	STD	STD 7	1			None		
9	STD 8	0	3	<Comment>	✓	STD	STD 8	1			None		
10	ICB	0	3	<Comment>	✓	QC		0.01			ICB	QC Next	
11	ICV	0	3	<Comment>	✓	QC	ICV STD	1			ICV	QC Next	
12	ICSA	0	3	<Comment>	✓	QC	ICSA	1			ICSA	QC Next	
13	ICSAB	0	3	<Comment>	✓	QC	ICSAB	1			ICSAB	QC Next	
14	FW 1	0	3	<Comment>	✓	UNKNOWN		1			None		FW
15	FW 2	0	3	<Comment>	✓	QC		1			DUP	QC Next	FW
16	FW spike 1	0	3	<Comment>	✓	QC	Matrix spike	1			MXS	QC Next	FW
17	FW spike 2	0	3	<Comment>	✓	QC	Matrix spike	1			MXS	QC Next	FW
18	Groundwater 1	0	3	<Comment>	✓	UNKNOWN		1			None		
19	Groundwater 2	0	3	<Comment>	✓	UNKNOWN		1			None		
20	Groundwater 3	0	3	<Comment>	✓	UNKNOWN		1			None		
21	Groundwater 4	0	3	<Comment>	✓	UNKNOWN		1			None		
22	CCB	0	3	<Comment>	✓	QC		1			CCB	QC Next	
23	CCV	0	3	<Comment>	✓	QC	CCV STD	1			CCV	QC Next	

Figure 5. Typical sample sequence set up within a Qtegra LabBook for automatic calculations of various QC samples including initial blank and calibration verification, DUP-QC, and interference check solutions

Concentrations													
	No	Date / Time	Sample Type	Label	23Na (KED AGD)	25Mg (KED AGD)	27Al (KED AGD)	39K (KED AGD m)	44Ca (KED AGD)	48Ti (KED AGD)			
1	1	9/8/2022 1:19:09 PM	BLK		9.754	0.502	1.088	-1.838	5.425	0.032			
2	2	9/8/2022 1:29:47 PM	STD										
10	10	9/8/2022 1:58:09 PM	QC - ICB	ICB	0.212	0.230	0.210	0.144	0.261	0.010			
11	11	9/8/2022 2:01:42 PM	QC - ICV	ICV	2,246.670 (99.9%)	2,324.840 (103.3%)	2,282.053 (101.4%)	2,184.228 (97.1%)	2,231.588 (99.2%)	99.671 (110.7%)			
12	12	9/8/2022 2:22:58 PM	QC - ICSA	ICSA	98,817.848 (98.8%)	92,749.325 (92.7%)	93,728.818 (93.7%)	96,840.298 (96.8%)	98,066.068 (98.1%)	1,982.977 (99.1%)			
13	13	9/8/2022 2:26:32 PM	QC - ICSAB	ICSAB	97,980.474 (98.0%)	99,850.061 (99.9%)	99,931.765 (99.9%)	101,307.265 (101.3)	100,031.068 (100.0)	1,958.949 (97.9%)			

Figure 6. View of concentration data and QC results automatically calculated within a Qtegra LabBook

Conclusion

The iCAP RQplus ICP-MS was extensively tested for compliance with EPA Method 6020B. The quality of the analytical data obtained over three consecutive days of measurements demonstrated that the built-in argon gas dilution system for controlled and automatic dilution of the sample aerosol is a powerful solution for laboratories analyzing demanding samples, such as soil digests or wastewater under high throughput conditions. The overall performance of the instrument suggests that reliable analysis of these type of samples can be performed without need of any maintenance and with no instrument downtime over three or more days of analytical work. Some of the important outcomes of this study are summarized below:

- All the requirements of EPA Method 6020B were met during the test period of three days, enabling the analysis of a total of 600 samples.
- The instrument detection limits (IDLs) and lower limits of quantification (LLOQs) achieved met and exceeded the requirements given in the method, which suggests that the employed methodology, with its optimized argon gas sample dilution, is suitable for achieving the required robustness and instrument sensitivity for these types of samples.
- Analyzing standard solutions containing concentrations above the highest point of the calibration according to section 9.6 of EPA Method 6020B established the wider linear range for each analyte (specifically up to $1,000 \text{ mg} \cdot \text{L}^{-1}$ for major elements like Na, K, Ca, Mg, Al, and Fe). This offers great flexibility for analyzing samples without the need for further dilution and improves productivity of the analytical laboratory. The wide linear range established for each analyte, with the optimized instrument settings that include AGD, enable the analysis of various environmental samples with wide concentration ranges within the same run.
- Results observed during analysis of ICB and CCB blank quality control samples indicated that the proposed method ensures minimum carryover between samples, enabling trouble-free measurement of high numbers of samples across the full calibrated concentration range.
- The accuracy obtained for ICV and CCV standard solutions over three consecutive days ensures the reliability and consistency of instrument performance while analyzing challenging high TDS containing samples, such as wastewater and solid waste digests.
- The analytical data obtained during analysis of interference check solutions (ICSA and ICSAB) highlight the effectiveness of single KED mode using helium as the collision gas in removing potential polyatomic interferences on each analyte, ensuring interference-free analysis every time.
- The data obtained during analysis of matrix-spiked and duplicate measurements demonstrated that minimum or no matrix effect was encountered when analyzing complex matrices such as wastewater.
- The observed behavior of the internal standards on three consecutive days of analysis highlights the robustness and consistency of the instrument performance. The consistent internal standard readback within the range of 75–125% suggests that the developed methodology is a reliable solution for effective handling of high-TDS-containing samples with no impact from the matrix content.
- The Qtegra ISDS Software provides all the necessary tools including different QC functions, automatic calculations, and limit and flag functionality to ensure that the analysis is performed as per the compliance requirements of EPA Method 6020B.

Reference

1. EPA Method 6020B. <https://www.epa.gov/sites/default/files/2015-12/documents/6020b.pdf>

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